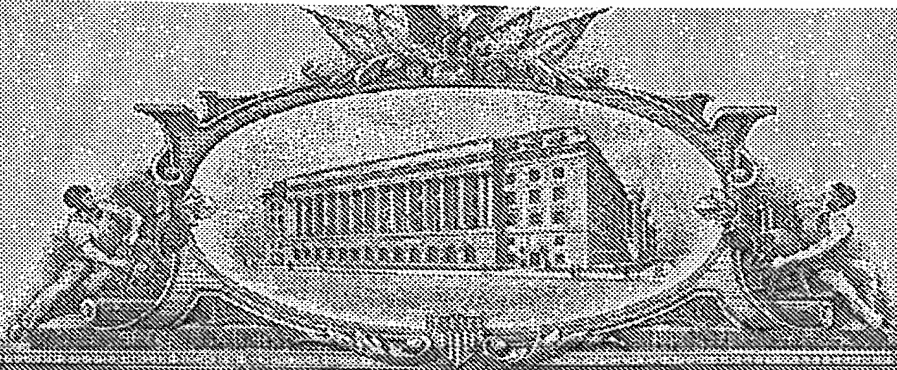


1219353



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME;

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

August 30, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/496,011
FILING DATE: *August 19, 2003*
RELATED PCT APPLICATION NUMBER: PCT/US04/24383

Certified by



Jon W Dudas

Acting Under Secretary of Commerce
for Intellectual Property
and Acting Director of the U.S.
Patent and Trademark Office

Post Available Copy

08/19/03 13281 U.S. PTO

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c).

19704 U.S. PTO
60/496011
08/19/03

Docket Number		63442-095	Type a plus sign (+) inside this box →	+
INVENTOR(s)/APPLICANT(s)				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (City and Either State or Foreign Country)	
BERSTED	Bruce	K.	Cumming GA 30040	
DOTY	James		Alpharetta GA 30022	
DECANNIERE	Jean		Brussels, BELGUIM	
DEHENNAU	Claude		Waterloo, BELGUIM	
WARKOSKI	Gregory		Cumming GA 30040	
ABUSLEME	Julio		Bollate (MI), ITALY	
TITLE OF THE INVENTION (280 characters max)				
HOLLOW BODY MADE FROM POLYPHTHALMIDE				
CORRESPONDENCE ADDRESS				
McDERMOTT, WILL & EMERY 600 13th Street, N.W. Washington, D. C. 20005-3096 (202) 756-8000				
STATE	Washington, D. C.	ZIP CODE	20005-3096	COUNTRY USA
ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/>	Specification	Number of pages [23]	<input type="checkbox"/>	Small Entity Statement
<input checked="" type="checkbox"/>	Drawings	Number of sheets [2]	<input type="checkbox"/>	Other (specify):
METHOD OF PAYMENT (check one)				
<input type="checkbox"/>	A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT (\$)
<input checked="" type="checkbox"/>	The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 500417			\$160.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

- ☒ No.
- ☐ Yes, the name of the U.S. Government agency and the Government contract number are:
- ☐ Additional inventors are being named on separately numbered sheets attached hereto.

Respectfully submitted,

McDERMOTT, WILL & EMERY

Bernard P. Codd

Bernard P. Codd
Registration No. 46,429

600 13th Street, N.W.
Washington, DC 20005-3096
(202) 756-8000 BPC:tlb
Facsimile: (202) 756-8087
Date: August 19, 2003

HOLLOW BODY MADE FROM POLYPHTHALAMIDE

BACKGROUND OF THE INVENTION

Polymeric hollow body articles have many uses including liquid handling and storage containers, hoses, tubing, and pipes. The use of polymeric hollow bodies, such as tubing and hoses, is increasing. One such application is motor vehicle fuel line tubing and hoses. At present these applications include the use of both monolayer and multilayer aliphatic polyamide (PA), high-heat rubber composites, and braided polytetrafluoroethylene (PTFE). At the same time there is also a trend toward higher temperatures in both diesel and passenger motor vehicle under-the-hood applications. While braided PTFE and high heat rubber composites can be used in these higher heat environments, the constructions are often complex and costly. The use aliphatic polyamide also has limitations in these high heat applications. In particular, PA12 has limitations with regard to both permeation of fuel and long term heat aging at the higher temperatures present in newer vehicles.

There are different requirements for the vapor return line and the liquid fuel line in today's fuel systems. In the vapor line, one of the primary requirements is the barrier property to prevent vapors from escaping into the environment, as well as the long-term thermal and mechanical requirements. Included in the mechanical requirements are sufficient flexibility and impact strength for both fabrication and safety. In addition to the requirements for vapor lines, liquid lines also include the requirement that essentially no components in the fuel line contaminates the fuel, which could lead to problems, such as clogged fuel injectors.

SUMMARY OF THE INVENTION

The invention disclosed herein demonstrates the manufacture and use of a hollow body having an outermost layer comprising polyphthalamide (PPA). As used herein,

"outermost layer" means the external layer of the hollow body; that is, there are no other layers of the hollow body immediately adjacent and external to the outermost layer. Hollow bodies within the scope of this invention include liquid storage and handling containers, tubing, pipes, and hoses. In particular, certain embodiments of the present invention are fuel line hoses for motor vehicles, aircraft, watercraft, recreational vehicles, and agricultural and industrial equipment including both liquid fuel delivery lines and vapor recovery lines.

Other certain embodiments of the present invention disclosed herein include the manufacture and use of a hollow body comprising an impact-modified polyphthalamide. Other certain embodiments of the present invention include hoses, such as fuel line hoses comprising a polyphthalamide and an impact modifier. The hoses included within the scope of this invention can be monolayer or multilayer hoses.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of a die used to extrude hoses according to embodiments of the invention.

FIG. 2 is an illustration of a die used to extrude multilayer hoses according to embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The polyamide compositions for hollow bodies that are compared in this disclosure are aromatic polyphthalamide compositions based on terephthalic acid, adipic acid, and optionally isophthalic acid, and hexamethylene diamine; PA12; and impact modified polyphthalamide (Examples 1-4). Data for permeation of various fluoropolymers and a liquid crystalline polymer (LCP) is also included for benchmarking the polyphthalamide compositions.

Certain embodiments of the invention comprise impact-modified polyphthalamide compositions. The impact modifiers comprise functionalized polyolefins. The functionalized polyolefin impact modifiers may comprise as little as 0.01 wt % carboxyl functionality. In certain embodiments of the invention, the functionalized polyolefin impact modifier comprises from about 0.1 weight % to about 5 weight % or greater carboxyl functionality. The functionalized polyolefins that may be used in certain embodiments of the present invention include those having a melt index in the range of about 0.5 to about 200 g/10 min. Any rubbery low-modulus functionalized polyolefin impact modifier with a glass transition temperature lower than 0 °C is suitable for this invention, including functionalized impact modifiers disclosed in U.S. Patent Nos. 5,436,294; to Desio et al. and 5,447,980; to Reichmann; the entire disclosures of which are incorporated herein by reference.

Suitable functionalized polyolefin impact modifiers are available from commercial sources, including maleated polypropylenes and ethylene-propylene copolymers available as EXXELOR™ PO and maleic anhydride-functionalized ethylene-propylene copolymer rubber comprising about 0.6 weight percent pendant succinic anhydride groups, such as EXXELOR® RTM. VA 1801 from the Exxon Mobil Chemical Company; acrylate-modified polyethylenes available as SURLYN®, such as SURLYN® 9920, methacrylic acid-modified polyethylene from the DuPont Company; and PRIMACOR®, such as PRIMACOR® 1410 XT, acrylic acid-modified polyethylene, from the Dow Chemical Company; maleic anhydride-modified styrene-ethylene-butylene-styrene (SEBS) block copolymer, such as KRATON® FG1901X, a SEBS that has been grafted with about 2 weight % maleic anhydride, available from Kraton Polymers; maleic anhydride-functionalized ethylene-propylene-diene monomer (EPDM) terpolymer rubber, such as ROYALTUF® 498, a 1% maleic anhydride functionalized EPDM, available from the Crompton Corporation. The

hollow bodies of the present invention are not limited to only those formed with these impact modifiers. Suitable functional groups on the impact modifier include any chemical moieties that can react with end groups of the polyphthalamide to provide enhanced adhesion to the high temperature matrix.

The amount of carboxyl-modified polyolefin impact modifier employed will be a quantity sufficient to impart sufficient tensile elongation at yield and break. Generally hollow bodies of certain embodiments of the present invention will comprise a polyphthalamide composition that comprises from about 2 weight % to about 40 weight % impact modifier. In certain other embodiments of the present invention the hollow bodies comprise a polyphthalamide composition comprising from about 15 weight % to about 30 weight % impact modifier. In certain embodiments of the present invention, the hollow bodies comprise a polyphthalamide composition that comprises about 25 weight % impact modifier, based on the weight of the polyphthalamide composition.

Alternative functionalized impact modifiers that may also be used in the practice of the invention include ethylene-higher alpha-olefin polymers and ethylene-higher alpha-olefin-diene polymers that have been provided with reactive functionality by being grafted or copolymerized with suitable reactive carboxylic acids or their derivatives such as, for example, acrylic acid, methacrylic acid, maleic anhydride or their esters, and will have a tensile modulus up to about 50,000 psi determined according to ASTM D-638. Suitable higher alpha-olefins include C₃ to C₈ alpha-olefins such as, for example, propylene, butene-1, hexene-1 and styrene. Alternatively, copolymers having structures comprising such units may also be obtained by hydrogenation of suitable homopolymers and copolymers of polymerized 1-3 diene monomers. For example, polybutadienes having varying levels of pendant vinyl units are readily obtained, and these may be hydrogenated to provide ethylene-

butene copolymer structures. Similarly, hydrogenation of polyisoprenes may be employed to provide equivalent ethylene-isobutylene copolymers.

Suitable dienes for use in the preparation of ethylene-alpha-olefin-diene terpolymers are non-conjugated dienes having 4 to about 24 carbon atoms, examples of which include 1,4-hexadiene, dicyclopentadiene and alkylidene norbornenes such as 5-ethylidene-2-norbornene. Mole fractions of ethylene units and higher alpha-olefin units in the ethylene-higher alpha-olefin copolymer rubbers generally range from about 40:60 to about 95:5. Ethylene-propylene copolymers having about 50 to about 95 mole percent ethylene units and about 5 to about 50 mole % propylene units are included among these. In terpolymers comprising polymerized diene monomer, the diene unit content can range up to about 10 mole %, and about 1 to about 5 mole % in certain embodiments. Also suitable are the corresponding block copolymers comprising two or more polymeric blocks, each formed of one or more monomers selected from ethylene and the higher alpha-olefin. The functionalized polyolefins will generally further comprise about 0.1 to about 10 weight percent functional groups.

Suitable polyphthalamides included within the scope of invention include any partially aromatic polyamide that contains aromatic moieties, as opposed to aliphatic polyamides like PA12, PA11, PA6, and PA66. Suitable polyphthalamides for certain embodiments of the present invention are formed by a polycondensation reaction between at least one aromatic dicarboxylic acid and a diamine. In certain embodiments, the aromatic dicarboxylic acid is terephthalic acid. In certain other embodiments of the present invention, the polyphthalamide further comprises isophthalic acid residues. In other certain embodiments of the present invention, the polyphthalamide is further formed from an aliphatic carboxylic acid, such as adipic acid. In certain other embodiments of the present

invention, the diamine is an aliphatic diamine comprising 4 to 12 carbon items, such as hexamethylene diamine (HMDA), nonane diamine, 2-methyl-1,5 pentadamine, and 1,4-diaminobutane. Suitable polyphthalamides for certain embodiments of the present invention are disclosed in previously referenced U.S. Patent Nos. 5,436,294; 5,447,980; and Re34,447 to Poppe et al., the entire disclosure of which is incorporated herein by reference.

In certain embodiments of the present invention, the dicarboxylic acid used in forming the polyphthalamide comprises a mole ratio of aromatic dicarboxylic groups in the range from at least about 50 mole % aromatic groups to about 100% aromatic groups. In certain embodiments of the present invention, the polyphthalamide polymer comprises from about 50 mole % to about 95 mole % hexamethylene terephthalamide units, from about 25 mole % to about 0 mole % hexamethylene isophthalamide units, and from about 50 mole % to about 5 mole % hexamethylene adipamide units. Suitable polyphthalamides for use in the present invention are available as AMODEL[®] A-1000, A-4000, A-5000, and A-6000 polyphthalamides from Solvay Advanced Polymers, LLC.

Certain polyphthalamide compositions used to form the hollow bodies of the present invention further comprise an external lubricant, such as PTFE or low density polyethylene (LDPE), to facilitate extrusion. Suitable powdered PTFE for certain embodiments of the present invention include POLYMIST[®] F5A available from Solvay Solexis.

Certain polyphthalamide compositions used to form hollow bodies of the present invention contain additives, including heat stabilizers. Suitable heat stabilizers include copper-containing stabilizers comprising a copper compound soluble in the polyphthalamide and an alkali metal halide. More particularly, in certain embodiments the stabilizer comprises a copper (I) salt, for example cuprous acetate, cuprous stearate, a cuprous organic complex compound such as copper acetylacetonate, a cuprous halide or the like, and an alkali

metal halide. In certain embodiments of the present invention, the stabilizer comprises a copper halide selected from copper iodide and copper bromide and an alkali metal halide selected from the iodides and bromides of lithium, sodium, and potassium. Formulations comprising copper (I) halide, an alkali metal halide and a phosphorus compound can also be employed to improve the stability of hollow bodies formed from polyphthalamide compositions during extended exposure to temperatures up to about 140 °C.

The amount of the stabilizer will generally be sufficient to provide a level of from about 50 ppm to about 1000 ppm copper. Certain polyphthalamide compositions comprise an alkali metal halide and copper (I) halide at a weight ratio the range of from about 2.5 to about 10, and most preferably from about 8 to about 10. Generally, the combined weight of copper and alkali metal halide compound in a stabilized polyphthalamide composition ranges from about 0.01 weight % to about 2.5 weight %. In certain other stabilized polyphthalamide compositions used to form hollow bodies according to the present invention, the stabilizer is present in the range of from about 0.1 weight % to about 1.5 weight %.

A suitable stabilizer for polyphthalamide compositions for forming hollow bodies according to the present invention comprises pellets of a 10:1 by weight mixture of potassium iodide and cuprous iodide with a magnesium stearate binder. The potassium iodide/cuprous iodide heat stabilizer provides protection against long term heat aging, such as exposure to under-the-hood automobile temperatures.

The hollow bodies of the present invention may further comprise a filler such as a reinforcing filler, structural fiber, or antistatic additive. Structural fiber useful in forming filled articles and composite products may include glass fiber, carbon or graphite fibers and fibers formed of silicon carbide, alumina, titania, boron and the like, as well as fibers formed from high temperature engineering resins such as, for example, poly(benzothiazole),

poly(benzimidazole), polyarylates, poly(benzoxazole), aromatic polyamides, polyaryl ethers and the like, and may include mixtures comprising two or more such fibers. Suitable fibers for certain embodiments of the present invention will be selected from glass fibers, carbon fibers and aromatic polyamide fibers such as the fibers sold by the DuPont Company under the trade name KEVLAR®.

Other fillers which may also be used in polyphthalamide compositions according to certain embodiments of the present invention to form hollow bodies include flake, spherical and fibrous particulate filler reinforcements and nucleating agents such as talc, mica, titanium dioxide, potassium titanate, silica, kaolin, chalk, alumina, mineral fillers, and the like. The fillers and structural fiber may be used alone or in any combination.

The polyphthalamide compositions used in certain embodiments of the hollow bodies of this invention may also be combined with pigments, dyes, fillers and the like as is commonly practiced in the resin arts, and these further additives may be employed alone or in any combination as needed. For particular applications, it may also be useful to include plasticizers, lubricants, and mold release agents, as well as thermal, oxidative and light stabilizers, and the like. The levels of such additives will be determined for the particular use envisioned, with up to about 50 weight %, based on total composition, of such additional additives considered to be within the range of ordinary practice in the extrusion art.

Table 1

Polyphthalamide Compositions				
	Examples			
Component	1	2	3	4
AMODEL [®] A-1004 PPA (wt. %)	75.75	74.75	74.18	73.18
maleic anhydride functionalized EPDM (wt. %)	0	25	0	25
maleic anhydride functionalized SEBS (wt. %)	24	0	24	0
10/1 KI/CuI stabilizer (wt. %)	0	0	1.57	1.57
Powdered PTFE (wt. %)	0.25	0.25	0.25	0.25
Total	100	100	100	100

Mechanical properties of some of the films formed from polyphthalamide compositions are given in Table 3. ISO 1BA tensile specimens were punched from the films. They were elongated at a crosshead speed of 0.5 mm/min and tested under the conditions of ISO 527. The impact modifiers provide polymer compositions that have higher average tensile elongation at yield and break over the unmodified control C1, as shown by Examples 1 and 2. The control C1 is unmodified AMODEL[®] A-1006 PPA. The PPA compositions comprising the impact modifier have tensile elongation at yield and break more than twice as high as the control. The higher tensile elongation at yield and break provides greater latitude in the processing parameters of the fuel hoses of the present invention.

Table 2

	Examples		
	1	2	C1
Impact Modifier	SEBS	EPDM	Unmodified
Test Temperature (°C)	23	23	23
Prior Conditioning	dry as molded	dry as molded	23 °C/50% RH
Average Tensile Elongation at Yield (%)	7.7	9.3	3.0
Average Tensile Elongation at Break (%)	154	169	66

FUEL PERMEATION TESTS

Fuel permeation tests were conducted on the examples, controls, and the comparative examples. The results of the fuel permeation tests are shown in Table 3. The fuel permeation tests were performed on films from the same specimens as those listed in Table 2.

In addition to impact modified PPA compositions, Examples 1 and 2, permeability measurements were also carried out on the following unmodified PPA compositions AMODEL[®] A-1006-C, A-4000, and A-6000. These film specimens were prepared by coextrusion between two peelable high density polyethylene (HDPE) layers.

Table 3

Examples	Average Thickness (μm)	CTF1 fuel at 60 °C, permeabilities in g.mm/m ² .day		
		Ethanol	Isooctane	Toluene
LCP	14	< 0.001	< 0.001	< 0.001
AMODEL [®] A-1006-C, annealed 165 °C /20 h	58	0.024	< 0.001	< 0.001
AMODEL [®] A-4000, annealed 160 °C /22.25 h	42	0.22	< 0.001	0.003
AMODEL [®] A-6000, annealed 165 °C /20 h	38	1.1	< 0.001	0.02
1	51	2.219	0.002	0.159
2	98	1.927	< 0.001	0.038
PA12 dry as molded	~45	> 125 (tentative)	17 (tentative)	> 177 (tentative)

The fuel tested is CTF1, a 45/45/10 by volume isooctane/toluene/ethanol blend. See standard SAE J1681 rev. Jan. 2000.

The measured fuel permeability is expressed as the number of grams of permeant that would permeate through a sheet of thickness 1 mm thickness and a surface area of 1 m² sheet in a 1 day period. The results obtained with a grade of LCP (liquid crystal polymer) exhibiting superior barrier properties are given for reference and illustrate detection limits of the method.

The permeability of the unmodified PPA is comparable to fluoropolymers. The permeability of the modified PPA, Examples 1 and 2, is superior to PA. PA12 is highly permeable and the steady-state was never reached. Ethanol and toluene began to seep very quickly after the test was launched and the cell rapidly became depleted of these species. Tentative permeability values were calculated from mass transfer measurements carried out at the beginning of the test via chromatography. The values tabulated are believed to be lower than the actual permeability values.

Table 4 summarizes permeability results measured at 60°C on various fluoropolymers. As can be seen in Tables 3 and 4, all the PPA compositions (annealed at 165°C or dry as molded) have fuel permeations comparable to the fluoropolymers and

superior to polyamides. Despite the fact that the incorporation of elastomers in the polyphthalamide compositions is generally detrimental to the barrier properties of PPA, especially as regards the alcohol and the aromatic components in the fuel, very good barrier properties are retained. As regards toluene and isooctane permeability, the elastomer modified polyphthalamide compositions are at least as good as the fluoropolymers listed in Table 4 and are superior to PA. For the ethanol component of CTF1 fuel at 60 °C, the modified polyphthalamides are only slightly less effective than the poly(vinylidene fluoride) (PVDF) homopolymer and ethylene--tetrafluoroethylene copolymer (ETFE), at least as good as the other fluoropolymers listed in Table 4, and superior to PA.

Table 4

Polymer	Thickness (μm)	Fuel	Isooctane (g.mm/m ² .day)	Toluene (g.mm/m ² .day)	Ethanol (g.mm/m ² .day)	Methanol (g.mm/m ² .day)
LCP, VECTRA [®] A950	25	CTF1	<0.01	<0.01	<0.02	-
PVDF, homopolymer SOLEF [®] 1010	50	CTF1	<0.01	0.85	1.3	-
PVDF, copolymer SOLEF [®] 61010	50	CTF1	0.2	6.6	7.1	-
TFE/HFP/VF2 terpolymer THV [™] 500G	50	CTF1	0.5	5.7	4.7	-
ETFE, TEFZEL [®] 280	50	CTF1	0.05	2.4	1.8	-
PCTFE, ACLAR [®] 33C	50	CTF1	0.4	5.6	2.3	-

The permeation results show that the unmodified PPA resins provide fuel permeation comparable to that of fluoropolymers. The presence of the elastomer in the impact modified polyphthalamide decreases the permeability, but the permeability is still far lower than that of the plasticized PA12 control

Extraction Data

While the leaching of components of polymeric fuel line components is less critical in vapor lines, the presence of such impurities in the liquid fuel line could lead to injector fouling. The solution used for the extraction study consisted of a mixture of 15% methanol and 85% of a 50/50 mixture of toluene/isooctane by volume (CM 15 fuel). The procedure for extraction comprised placing 15 grams of pellets in 80 ml of agitated liquid at 40 °C for 168 hours, and measuring the dried residue of the decanted solution. The percent extractables for Examples 1 and 2 were measured to be 0.17 and 0.20 % respectively. While not zero, the extractable values are surprisingly low compared to the 8 to 12 % extractables that would be expected for plasticized PA12 currently used as a monolayer hoses.

Heat Aging Comparisons With PA12

Resistance to long term heat aging is considered extremely important to the viability of using polymers in fuel lines with the ever increasing temperature requirements in automobiles. A comparison of heat stabilized versions of Examples 3 and 4 with heat stabilized PA12 is provided in Table 5.

Table 5

Examples	Izod Impact (ft-lbs/in.) Strength After 255 Hours at Temperature			
	23 °C (Initial)	140 °C	150 °C	160 °C
PA12	20.46	0.67	0.69	0.16
3	19.73	17.07	15.02	12.47
4	19.8	17.07	14.99	11.77

As can be seen the PA12 undergoes a catastrophic loss in Izod impact strength after heat aging. Consequently, the partially aromatic impact modified polyamides are a much safer choice for retention of impact properties after long term exposure to elevated temperatures in the presence of air.

Manufacture Of Hoses From Impact Modified Polyphthalamide

Hoses were manufactured using a Scamex 30 mm single screw extruder with a die that had been adapted to it. The hoses produced were 8 mm OD X 6 mm ID. The die used is shown in FIG. 1. In certain embodiments of the present invention the die temperatures used was 320°C. Listed in Tables 6 and 7 are dimensions for a number of sample hoses, made according to embodiments of the present invention, demonstrating that suitable fuel line hoses are produced from impact modified partially aromatic polyamides according to the present invention.

Impact modified hoses can be produced by preblending the polyphthalamide and the impact modifier in a melt and forming pellets of the polymer blend. The pellets of preblended impact modified polyphthalamide can then be extruded into hoses as required. Alternatively, the impact modifier and the polyphthalamide can be added as separate components into the extruder and blended together during the extrusion process.

Table 6**Example 1**

Average outer diameter (mm)	Average thickness (mm)	OD minimum (mm)	OD maximum (mm)	Minimum thickness (mm)	Maximum thickness (mm)
8.12	1.11	8.11	8.13	1.08	1.13
8.15	1.07	8.10	8.22	0.95	1.19
8.09	1.03	8.04	8.12	0.98	1.11
8.16	1.08	8.15	8.17	1.04	1.11
8.09	1.09	8.06	8.12	1.04	1.12
8.13	1.10	8.10	8.15	1.04	1.15
8.11	1.13	8.08	8.14	1.08	1.16
8.16	1.18	8.12	8.18	1.14	1.23
8.10	1.11	8.08	8.12	1.04	1.20

Table 7**Example 2**

Average outer diameter (mm)	Average thickness (mm)	OD minimum (mm)	OD maximum (mm)	Minimum thickness (mm)	Maximum thickness (mm)
8.10	1.17	8.08	8.12	1.14	1.22
8.09	1.13	8.07	8.12	1.09	1.15
8.07	1.05	8.06	8.09	1.02	1.08
8.04	1.07	8.00	8.07	1.03	1.11
8.12	0.88	8.08	8.15	0.76	0.99
8.09	0.99	8.07	8.12	0.84	1.05
8.09	1.00	8.04	8.15	0.86	1.06
8.08	1.09	8.07	8.09	1.02	1.16

The hose made from the Example 2 composition was pushed onto a connector without splitting, which is a requirement for fuel line connector hose. The hose must be elongated by about 50 % in order to be pushed onto the connector.

In certain embodiments of the present invention, the hollow body comprises a monolayer structure of a polyphthalamide composition. As used herein, a "monolayer" is formed from single layer of a polymer composition wherein the polymer composition is

substantially the same across the entire thickness of the layer. In certain embodiments of the present invention, the thickness of the monolayer can range from about 500 microns to about 12.5 mm. In certain embodiments of the present invention, the monolayer thickness ranges from about 750 microns to about 7 mm.

If the possibility exists of components of the PPA hollow body leaching into a liquid in the hollow body, such as leaching into the fuel in a fuel hose line, certain embodiments of the present invention comprise a multilayer hose construction that include a substantially chemically inert inner layer. For example, an inner layer of a fluoropolymer can be coextruded with the PPA composition outer layer to produce a liquid fuel hose with a chemically inert inner layer. The fluoropolymer inner layer can be relatively thin layer compared to the PPA layer. The thickness of the fluoropolymer layer can range from about 5 microns to about 700 microns. In certain embodiments of the present invention, the thickness of the fluoropolymer layer ranges from about 100 to about 700 microns. In other certain embodiments, the thickness of the fluoropolymer ranges from about 300 microns to about 500 microns. The thickness of the PPA composition outer layer ranges from about 500 microns to about 12.5 mm. In certain embodiments of invention, the thickness of the polyphthalamide composition outer layer ranges from about 750 microns to about 7 mm.

The fluoropolymer can be any substantially chemically inert fluoropolymer. Where the hollow body is a hose, the fluoropolymers used according to the present invention will be capable of being coextruded with PPA into thin layers. Thus, the fluoropolymer must also be able to withstand the melt temperature of the polyphthalamide. Suitable fluoropolymers for use as an inner layer in certain embodiments of the hollow body according to the present invention include poly(vinylidene fluoride) (PVDF) available as SOLEF[®] from Solvay Solexis, ethylene--tetrafluoroethylene copolymers (ETFE) available as TEFZEL[®] from

DuPont, poly(chlorotrifluoroethylene) (PCTFE) available as ACLAR[®] from Honeywell or ethylene-chlorotrifluoroethylene copolymers (ECTFE) available as HALAR[®] from Solvay Solexis, and perfluorinated ethylene-propylene copolymers (FEP) available as DYNEON[™] FEP from 3M or TEFLON[®] FEP from DuPont.

Hollow bodies according to this invention can comprise a number of coextruded layers. For example, as described above, a multilayer hose with a chemically inert inner layer can be extruded. Additional layers can be coextruded, if necessary for applications that require three or more layers. A die for coextruding three layers is illustrated in FIG. 2.

Other certain embodiments of the present invention include fossil fuel powered motor devices comprising any of the hollow bodies, such as fuel hose lines, described herein. Fossil fuel powered motor devices, as used herein, include motor vehicles, aircraft, watercraft, recreational vehicles, and agricultural and industrial equipment. In certain embodiments of the present invention, the motor vehicles include automobiles, motorcycles, buses, and trucks.

The embodiments described in the instant disclosure are for illustrative purposes only. They should not be construed to limit the claims. As is clear to one of ordinary skill in this art, the instant disclosure encompasses a wide variety of embodiments not specifically illustrated herein.

WHAT IS CLAIMED IS:

1. A hollow body having an outermost layer, wherein the outermost layer comprises a polyphthalamide composition.
2. A hollow body comprising a polyphthalamide and an impact modifier.
3. The hollow body according to either claim 1 or 2, further comprising an external lubricant.
4. The hollow body according to claim 3, wherein the external lubricant comprises polytetrafluoroethylene or low density polyethylene.
5. The hollow body according to any of claims 1 to 4, wherein the polyphthalamide is formed from at least one dicarboxylic acid and at least one diamine and the dicarboxylic acid comprises at least about 50 mole % aromatic dicarboxylic acid.
6. The hollow body according to claim 5, wherein the dicarboxylic acid comprises up to 100 mole % aromatic dicarboxylic acid.
7. The hollow body according to claim 2, wherein the impact modifier is a rubber.
8. The hollow body according to claim 7, wherein the rubber is a functionalized polyolefin-based rubber.
9. The hollow body according to claim 8, wherein the functionalized polyolefin-based rubber is a maleic anhydride functionalized styrene-ethylene-butylene-styrene block copolymer.

10. The hollow body according to claim 8, wherein the functionalized polyolefin based rubber is a maleic anhydride functionalized ethylene-propylene-diene monomer rubber.

11. The hollow body according to any of claims 1 to 10, further comprising a substantially chemically inert inner layer.

12. The hollow body according to claim 11, wherein the substantially chemically inert inner layer comprises a fluoropolymer.

13. The hollow body according to claim 12, wherein the fluoropolymer is selected from the group consisting of poly(vinylidene fluoride), ethylene--tetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, and perfluorinated ethylene-propylene copolymers.

14. The hollow body according to any of claims 1 to 13, wherein the polyphthalamide is formed from terephthalic acid and an aliphatic diamine.

15. The hollow body according to any of claims 1 to 13, wherein the polyphthalamide is formed from terephthalic acid, an aliphatic dicarboxylic acid, and an aliphatic diamine.

16. The hollow body according to claim 14, wherein the polyphthalamide is further formed from isophthalic acid.

17. The hollow body according to claim 15, wherein the polyphthalamide is further formed from isophthalic acid.

18. The hollow body according to either claim 14 or 16, wherein the aliphatic diamine is hexamethylene diamine.
19. The hollow body according to either claim 15 or 17, wherein the aliphatic dicarboxylic acid is adipic acid and the aliphatic diamine is hexamethylene diamine.
20. A hose having an outermost layer, wherein the outermost layer comprises a polyphthalamide composition.
21. A hose comprising a polyphthalamide and an impact modifier.
22. The hose according to either claim 20 or 21 further comprising an external lubricant.
23. The hose according to claim 22, wherein the external lubricant comprises polytetrafluoroethylene or low density polyethylene.
24. The hose according to any of claims 20 or 23, wherein the polyphthalamide is formed from at least one dicarboxylic acid and at least one diamine and the dicarboxylic acid comprises at least 50 about mole % aromatic dicarboxylic acid.
25. The hose according to claim 24, wherein the dicarboxylic acid comprises up to 100 mole % aromatic dicarboxylic acid.
26. The hose according to claim 21, wherein the impact modifier is a rubber.
27. The hose according to claim 26, wherein the rubber is a functionalized polyolefin-based rubber.

28. The hose according to claim 27, wherein the functionalized polyolefin-based rubber is a maleic anhydride functionalized styrene-ethylene-butylene-styrene block copolymer.

29. The hose according to claim 27, wherein the functionalized polyolefin based rubber is a maleic anhydride functionalized ethylene-propylene-diene monomer rubber.

30. The hose according to any of claims 20 to 29, wherein the hose is a multilayer hose.

31. The hose according to any of claims 21 to 29, wherein the hose is a monolayer hose.

32. The hose according to any of claims 20 to 30, further comprising a substantially chemically inert inner layer.

33. The hose according to claim 32, wherein the substantially chemically inert inner layer comprises a fluoropolymer.

34. The hose according to claim 33, wherein the fluoropolymer is selected from the group consisting of poly(vinylidene fluoride), ethylene--tetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene--chlorotrifluoroethylene copolymers and perfluorinated ethylene-propylene copolymers.

35. The hose according to any of claims 20 to 34, wherein the polyphthalamide is formed from terephthalic acid and an aliphatic diamine.

36. The hose according to any of claims 20 to 34, wherein polyphthalamide is formed from terephthalic acid, an aliphatic dicarboxylic acid and an aliphatic diamine.

37. The hose according to claim 35, wherein the polyphthalamide is further formed from isophthalic acid.

38. The hose according to claim 36, wherein the polyphthalamide is further formed from isophthalic acid.

39. The hose according to either claim 35 or 37, wherein the aliphatic diamine is hexamethylene diamine.

40. The hose according to either claim 36 or 38, wherein the aliphatic dicarboxylic acid is adipic acid and the aliphatic diamine is hexamethylene diamine.

41. The hose according to any of claims 20 to 40, wherein the hose is a fuel line hose.

42. A fossil fuel powered device comprising the fuel line hose of claim 41.

43. The fossil fuel powered device according to claim 42, wherein the fossil fuel powered device is selected from the group consisting of motor vehicles, aircraft, watercraft, and agricultural and industrial equipment.

44. The motor vehicle of claim 43, wherein the motor vehicle is an automobile.

ABSTRACT OF THE DISCLOSURE

Hollow bodies made from polyphthalamide are suitable for forming fuel line hoses for both liquid fuel delivery and fuel vapor recovery. For improved tensile elongation the hollow bodies can additionally comprise an impact modifier. Fuel line hoses formed from polyphthalamide and impact modified polyphthalamide provide improved resistance against permeation of fuel components and superior heat aging characteristics over commonly used aliphatic polyamides. In certain embodiments of the fuel hose, a substantially chemically inert inner layer is provided to prevent possible leaching of polyphthalamide polymer composition components into liquid fuel.

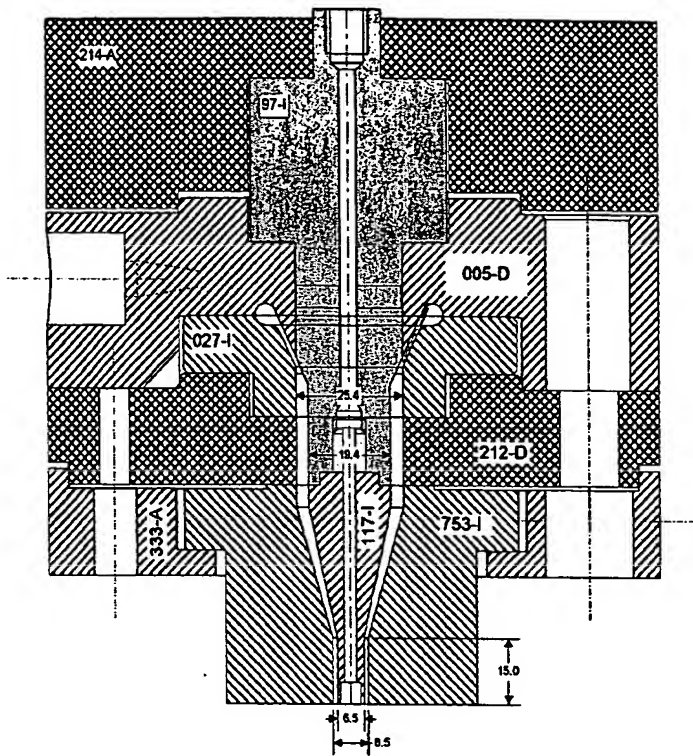


FIG. 1

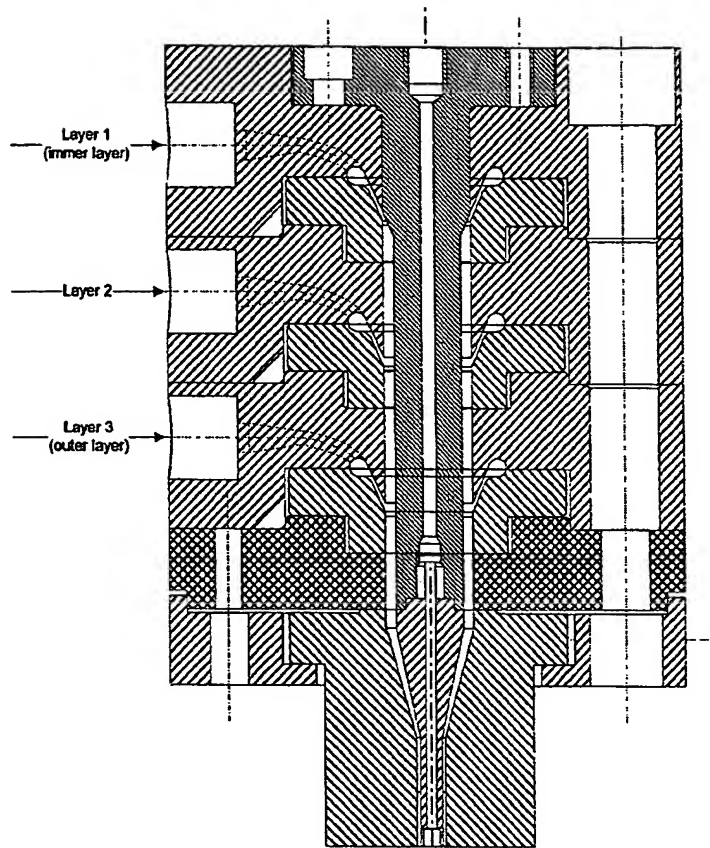


FIG. 2

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/024383

International filing date: 17 August 2004 (17.08.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/496,011
Filing date: 19 August 2003 (19.08.2003)

Date of receipt at the International Bureau: 06 September 2004 (06.09.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse